On the Recombination of the Ions Produced by Röntgen Rays in Gases and Vapours.

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1. *Introductory.*

In a space containing both positive and negative ions the concentration of the ions tends to diminish as a result of the union of ions of opposite sign. The number of ions of each sign which disappear in unit time is proportional to the number of collisions between ions of opposite sign. This is proportional to the product of the concentrations of the two kinds of ions and it is customary to express the change in the form of the equation

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}, \tag{1}$$

where n_1 and n_2 are the numbers of positive and negative ions respectively in unit volume, and α is a constant for a gas at a given temperature and pressure; α is called the coefficient of recombination of the ions.

When the concentrations of the two kinds of ions are equal the equation takes the simple form

$$\frac{dn}{dt} = -\alpha n^2,$$

the solution of which is

$$\frac{1}{n} - \frac{1}{n_0} = \alpha t, \tag{2}$$

n_0 being the concentration of the ions initially, and n the concentration after an interval of time t. In what has been said above the effect of diffusion is supposed to be negligible.

The coefficient of recombination is of fundamental importance in the theory of the ionisation of gases, and an experimental verification of equation (2) serves as a general test of the theory. Methods of measuring the coefficient have been devised by Rutherford,* Townsend,† Langevin,‡ and others, and many determinations have been made by different observers.§ The results obtained present some rather wide divergences, both as regards the absolute values of the coefficient of recombination at a given pressure, and also as regards the manner in which the coefficient varies when the pressure is changed. Thus McClung found a constant value for α for pressures varying from 0·125 to 3 atmospheres, whereas Langevin, in some experiments on air, found that, for a range of pressures from 760 mm. to 250 mm., α was approximately proportional to the pressure.

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* Rutherford, 'Phil. Mag.,' 1897, vol. 44, p. 422.

† Townsend, 'Phil. Trans.,' 1899, vol. 193, p. 129.

‡ Langevin, 'Annales de Chimie et de Physique,' 1903, vol. 28, p. 433.

§ McClung, 'Phil. Mag.,' 1902, vol. 5, p. 283; Hendren, 'Phys. Rev.,' 1905, vol. 21, p. 314; Retschinsky, 'Ann. der Physik,' 1906, 4, vol. 17, p. 518.

In view of these divergences, of the fact that no work had been done on vapours, and of the importance of the subject from a theoretical point of view, it was thought that an investigation of the coefficient of recombination of ions in gases and vapours at different pressures would prove a fruitful subject for research.

The work of Bragg and Plimpton has shown that certain peculiarities occur in the initial stages of recombination. It was the author's aim to measure the coefficient when the initial peculiarities have been dissipated, these being the only conditions under which the coefficient has a simple meaning. In this paper is given an account of the work which has been done on some gases and vapours. The measurements on vapours are still in progress.

2. *Experimental Method.*

The methods devised by Rutherford and used by him, McClung and others, are by far the simplest of those that have been employed for the measurement of the coefficient of recombination. However, they serve to verify the law of recombination only in the simple case in which the concentrations of the positive and negative ions are equal. Moreover, in practice, they are subject to certain difficulties. In the first place, the source of ionisation (Röntgen rays in this case) must act for some time, and it is assumed that the source remains of constant intensity. This condition is one which it is notoriously difficult to satisfy, especially in the case of a bulb giving out penetrating rays. In consequence of this the values are liable to present wide divergences, and there is some difficulty in weighing up the results. In the second place, the distribution of the ionisation in the vessel is of no small importance. On account of the secondary radiation which is always present in these experiments, and which may produce intense local ionisation, it is impossible to know in an exact manner the distribution of the ionisation in the vessel. Finally, the effects of the diffusion of the ions to the walls of the vessel are important, and there is some difficulty in correcting for this effect. Langevin* has shown the importance of diffusion in McClung's experiments. At ordinary pressures diffusion accounted for about 10 per cent. of the observed recombination, and, at a pressure of one-eighth of an atmosphere, the values obtained were probably five or six times too large. In Langevin's method these are avoided, and this was the one used throughout these experiments.

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* 'Journ. de Physique,' 1905, vol. 4, p. 322.

Before giving a short account of the method, it may be useful to consider the significance attached by Langevin to the term "number of collisions." Suppose that round each negative ion in an ionised gas a surface is described, the dimensions of which are arbitrary, except that its largest dimension is large compared with the mean free path of an ion, and small compared with average distance between two ions. The number of positive ions which, in a time dt, penetrate into the interior of these surfaces, as a result of the attraction of the negative ions inside, is independent of the dimensions of the surface and of the electric field existing in the gas due to the neighbouring conductors. This number Langevin defines to be the number of collisions between ions of opposite sign in the time dt.

The number of these collisions is given by the expression

$$4\pi (k_1 + k_2) n_1 n_2 e \, dt,$$

in which k_1 and k_2 are the mobilities of the positive and negative ions respectively, n_1 and n_2 are the concentrations of the positive and negative ions, and e is the charge on an ion of either sign. This expression contains neither the dimensions of the surface supposed to surround the ion nor the strength of the electric field.

If each collision results in a recombination of the two ions, the rate of change of the concentration of the positive and negative ions will be equal to

$$4\pi (k_1 + k_2) n_1 n_2 e.$$

But recombination does not necessarily follow a collision. The initial kinetic energy of the ions, supplemented by the energy due to their mutual attraction, may be so great that the two ions separate again after having approached, or even after having gravitated the one round the other. A fraction ϵ only, necessarily less than unity, of the number of collisions will result in recombination, so that we have

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = -4\pi\epsilon (k_1 + k_2) e n_1 n_2.$$

Comparing this with the expression

$$\frac{dn_1}{dt} = \frac{dn_2}{dt} = -\alpha n_1 n_2,$$

we have

$$\epsilon = \frac{\alpha}{4\pi (k_1 + k_2) e}.$$

In the method described below, this ratio is measured directly under variable conditions. If the laws of recombination and mobilities are exact, the experiment, for a given gas under given conditions of temperature and pressure, ought to furnish for this ratio a constant value, independent of the exterior field and of the intensity of the ionisation. This fraction having been measured and the mobilities of the ions being known, the coefficient of recombination can be deduced.

There remains to be considered the method of measuring this ratio. The principle is as follows:—Suppose we have two parallel plates A and B, and a uniform field in the region between the plates, the direction of the field being from B to A. Let the gas between the plates be ionised by a single flash, of very short duration, from a Röntgen-ray bulb. During the flight of the ions to the two plates there will be a certain number of collisions, and the positive charge which finally reaches the plate A will, for a given initial charge present in the gas, depend on the number of these collisions. Increasing the electric field between the plates decreases the time of flight and therefore the number of collisions, with a consequent increase in the charge on A.

In the case where the total charge Q_0 of either sign, produced in the gas by the single flash of Röntgen rays, is so small that the moving charges do not sensibly modify the field, Langevin has calculated the charge Q received by the plate A and shown that it does not depend on the distribution of the ions between the plates. This quantity is given by the expression

$$\frac{\epsilon Q}{\sigma} = \log_e\left(1+\frac{\epsilon Q_0}{\sigma}\right),$$

in which σ is determined by the relation $X = 4\pi\sigma$, X being the strength of the electric field between the plates. For the proof of this the reader is referred to the original memoir.

Determination of ϵ.—In order to find ϵ, the charges Q_1 and Q_2, received by the plate for different values of the electric field with the same initial ionisation, are measured. If the electric fields are X_1 and X_2, the expressions for Q_1 and Q_2 are

$$\frac{\epsilon Q_1}{\sigma_1} = \log\left(1+\frac{\epsilon Q_0}{\sigma_1}\right) \quad \text{and} \quad \frac{\epsilon Q_2}{\sigma_2} = \log\left(1+\frac{\epsilon Q_0}{\sigma_2}\right), \tag{3}$$

in which $X_1 = 4\pi\sigma_1$ and $X_2 = 4\pi\sigma_2$.

Experiment gives the relative values of the quantities Q_1, Q_2, σ_1, σ_2. Q_1 and Q_2 are proportional to the quantities of electricity received by the electrode in the two cases after one discharge from a Crookes tube, and σ_1 and σ_2 are proportional to the quantities of electricity induced on the electrode at the instant when the electric field is established.

The simplest method of calculating ϵ has been found to be a graphical one, due to Langevin. For convenience of explanation later, it will be convenient to describe this briefly here. Writing

$$x = \frac{\epsilon Q_0}{\sigma_2}, \qquad y = \frac{Q_2}{Q_0},$$

the equations (3) become

$$y = \frac{1}{x}\log(1+x) \quad \text{and} \quad y\frac{Q_1}{Q_2} = \frac{\sigma_1}{x\sigma_2}\log\left(1+\frac{x\sigma_2}{\sigma_1}\right),$$

in which Q_1, Q_2, σ_1 and σ_2 appear only in the ratios Q_2/Q_1 and σ_2/σ_1.

x and y being known, we have

$$\epsilon = xy\frac{\sigma_2}{Q_2}.$$

A curve is now drawn with log x as abscissæ and log y as ordinates, y being given by the relation

$$y = \frac{1}{x}\log(1+x).$$

The points corresponding to x and $x\sigma_2/\sigma_1$ have a known difference of abscissæ

$$\log x - \log\frac{x\sigma_2}{\sigma_1} = \log\frac{\sigma_1}{\sigma_2}.$$

The corresponding ordinates are log y and log yQ_1/Q_2 and their difference is also a known quantity

$$\log y - \log y\frac{Q_2}{Q_1} = \log\frac{Q_1}{Q_2}.$$

In order to determine x and y, it is sufficient to determine on the curve two points P and P′, the abscissæ and ordinates of which differ respectively by the known quantities log σ_1/σ_2 and log Q_1/Q_2. By moving a transparent paper over the curve it is possible to find these points with both ease and accuracy.

The abscissæ and ordinates of these points are log x and log y, and we have

$$\log\epsilon = \log x + \log y + \log\sigma_2 - \log Q_2.$$

An example will illustrate this. In an experiment on dry carbon dioxide at a pressure of 614 mm. of mercury and a temperature of 13·5° C., the following results were obtained :—

$$\log Q_1 = 2{\cdot}69020, \qquad \log\sigma_1 = 2{\cdot}2954,$$
$$\log Q_1/Q_2 = 0{\cdot}02927, \qquad \log\sigma_1/\sigma_2 = 0{\cdot}3945.$$

The values of x and y obtained from the curve were

$$\log x = \bar{1}\cdot 400, \qquad \log y = 1\cdot 950.$$

Hence $\log \epsilon = \bar{1}\cdot 5900$ and ϵ is equal to 0·39.

In this method it will be noticed (1) that the distribution of the ionisation is unimportant, (2) that the effect of diffusion is negligible, and (3) that there is no need of a constant source of radiation. This last condition was, however, fairly easily obtained with the special arrangement used for producing the break in the primary current of the induction coil.

3. *Experimental Arrangement.*

The diagram of the connections and the disposition of the apparatus is given in fig. 1. In the main it is the same as that used by Langevin, but certain necessary modifications were introduced. A momentary discharge was produced in the Röntgen-ray bulb by the breaking of the contact at T, which was in the primary circuit of a Marconi induction coil. The contact at T was between two pieces of platinum which could be separated very suddenly. For effective action at this break it was necessary to have the platinum pieces held together by a steady, firm pressure. A capacity of about 8 microfarads was inserted in order to suppress the spark which would occur when the circuit

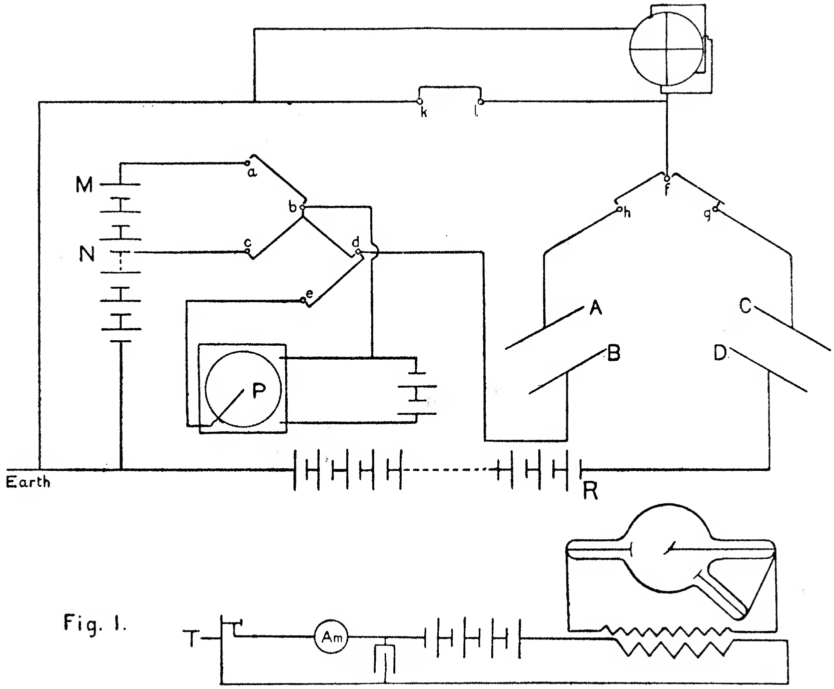

Fig. 1.

was broken. A small spark here gave great irregularities in the Röntgen-ray flash; however, when this was entirely eliminated, and with a constant current, as measured by the ammeter, in the primary, the ionisation produced in the chamber by a single flash of rays was very constant, and readings could be repeated with great ease.

The ionisation chambers are denoted by AB and CD. The upper electrodes A and C, by means of a key, could be connected, either separately or together, with the insulated pair of quadrants of the electrometer. Two exactly similar ionisation chambers were used and the Röntgen-ray bulb was adjusted so that the ionisation produced in each chamber by a single flash of the rays was the same. With electric fields of opposite sign in the two chambers, the electric charge received by the electrometer when connected with both chambers was zero. The quantity received in either of these chambers gives the charge Q_2.*

If the electric field in one chamber be now increased, one electrode receives a quantity of electricity Q_1 and the other a quantity Q_2 of opposite sign. If the two electrodes are both connected to the electrometer, the latter will suffer a deflection proportional to the difference of these charges, that is to Q_1-Q_2. This difference is a very small fraction of either of the charges Q_1 or Q_2 and the error in ϵ is approximately proportional to the error in Q_1-Q_2. It is better, therefore, to measure Q_1-Q_2 and Q_1 rather than Q_1 and Q_2 separately. Q_1-Q_2 may be only 1 or 2 per cent. of Q_1, and some special device is necessary if both quantities are to be measured with the same electrometer.

Langevin used an electrometer with a condenser of variable capacity. A similar method was first tried in these experiments but was not found to be very satisfactory. The variable capacity employed consisted of two sets of 10 parallel plates fixed to two axes. One set, which was connected with the electrometer, remained fixed; the other, which was kept at zero potential, could be rotated into or out of the fixed set, thus increasing or decreasing the capacity. In measuring the quantity Q_1, the condenser was closed and the deflection of the electrometer observed when only one chamber was connected and a single flash used. At the same time a charge Q_2 of opposite sign had been communicated to the second chamber. This chamber was then connected to the electrometer, which gave a small deflection proportional to the charge $Q_1 - Q_2$. The movable set of plates of the condenser was revolved so as to decrease the capacity of the system. The deflection was now much greater and could be easily measured.

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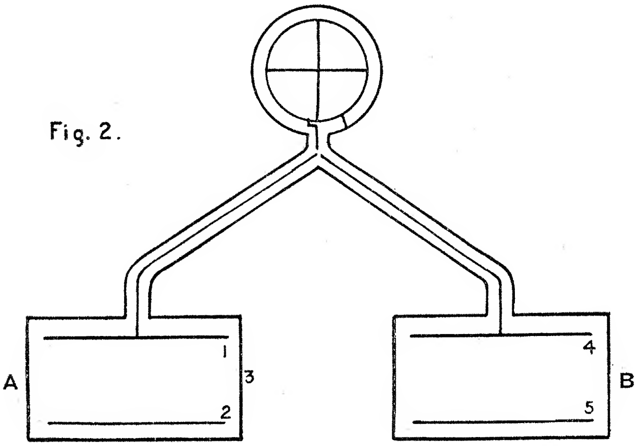
* The accumulation of the ions in the neighbourhood of the electrodes affects the electric field, which is no longer uniform but is of greater intensity in the vicinity of the electrodes. In the case of a uniform ionisation between the electrodes, Langevin has shown that the relative error resulting from the modification of the field by the ions has for its principal term and, at the same time, its upper limit, the value $Q_0/24\sigma$. The error, therefore, will be less than 1 per cent. so long as Q_0 does not exceed $\frac{1}{4}\sigma$. With a non-uniform ionisation the modification of the field by the ions becomes more important. At low pressures with small values of Q_1 and Q_2, Q_1-Q_2 becomes very small, and it is necessary to have larger values of the ratio Q/σ. In general, however, voltages were chosen so as to render the effect of the ionisation on the field practically negligible.

In using this method one serious difficulty was experienced which it was found impossible to eliminate entirely. This was an effect due to contact difference of potential. If the electrometer and large capacity system, initially connected to earth and then insulated, had its capacity decreased by opening the condenser, a deflection was always produced in the electrometer. Careful attention to the plates, etc., failed to eliminate this effect entirely. Apparently there was always a small difference of potential (probably some form of contact difference); and, on decreasing the capacity, this was revealed by the increased deflection. In certain cases this effect was an appreciable fraction of the deflection due to the charge $Q_1 - Q_2$. On this account another method was employed in which a variable condenser was done away with. All the charges to be measured were compensated by means of charges which were induced on the upper electrodes by varying the potential of the lower electrodes. The only quantities to be measured were potentials.

The method used was as follows:—

Fig. 2.



In fig. 2, A and B are the ionisation chambers. The plates 1 and 4 can be connected, either separately or together, to the electrometer, and the potential of the lower plate 2 can be varied. The outer case of the ionisation chambers, the guard tubes T and T_1, one pair of quadrants, and the case of the electrometer, form part of one conductor kept at zero potential throughout the experiment. Suppose that, due to a single flash of Röntgen rays, the plate 1 receives a charge Q_1 and the plate 4 a charge Q_2. The quantities to be measured are the ratios $(Q_1-Q_2)/Q_1$ and Q_1/σ_1, where $4\pi\sigma_1 = X_1$, the electrostatic field between the plates 1 and 2 of the first chamber. Let q_{11}, q_{21},..., be the coefficients of capacity and induction of the systems of conductors, the suffixes referring to the numbers in the figure.

Let the plate 1 and the electrometer be insulated and the plate 4 be disconnected; the charge Q_0 on the conductor 1 is given by the relation

$$Q_0 = q_{11}V_1+q_{21}V_2+q_{31}V_3,$$

in which V_1, V_2 and V_3, are the potentials of 1, 2 and 3, respectively. Initially, V_1 and V_3 are both zero, so that the equation may be written

$$Q_0 = q_{21}V_2. \tag{4}$$

When the charge Q_1 is given to 1, let the potential of the electrometer become v. Then we have

$$Q_0+Q_1 = q_{11}v+q_{21}V_2. \tag{5}$$

Suppose now that the potential of 2 is changed to V_2+u, and that, in consequence, the potential of the electrometer becomes v_1, then, since there is no increase in the charge on 1, we have

$$Q_0+Q_1 = q_{11}v_1+q_{21}(V_2+u),$$

whence, subtracting (4),

$$Q_1 = q_{11}v_1+q_{21}u.$$

If u be adjusted so that the potential of the electrometer is brought back to zero, then

$$Q_1 = q_{21}u. \tag{6}$$

Similarly, when 1 and 4 are both connected to the electrometer

$$Q_0' = q_{11}V_1+q_{21}V_2+q_{54}V_4+q_{44}V_1,$$

and therefore

$$Q_0' = q_{21}V_2+q_{54}V_4, \quad \text{since } V_1 \text{ is zero.} \tag{7}$$

When the charge Q_1-Q_2 is given to 1, let the potential of the electrometer become v'. Then we have

$$Q_0'+(Q_1-Q_2) = q_{11}v'+q_{44}v'+q_{21}V_2+q_{54}V_4.$$

Suppose now, that the potential of 2 is changed to $V+u'$, and that the electrometer, in consequence, assumes a potential v_2'. We have

$$Q_0'+(Q_1-Q_2) = q_{11}v_2'+q_{44}v_2'+q_{21}(V_2+u')+q_{54}V_4, \tag{8}$$

and subtracting (7) from (8),

$$Q_1-Q_2 = q_{11}v_1'+q_{44}v_1'+q_{21}u'.$$

If u' be adjusted so that the potential of the electrometer is brought back to zero, this relation becomes

$$Q_1 - Q_2 = q_{21}u'. \tag{9}$$

Combining (6) with (9) we get the simple relation

$$\frac{Q_1 - Q_2}{Q_1} = \frac{u'}{u}. \tag{10}$$

Thus the ratio of the two charges is equal to the ratio of the potentials necessary to bring the potential of the electrometer back to zero in the two cases.

Again, in measuring the ratio Q_1/σ_1, connect 1, 2, 3, and 4 to earth, and then insulate 1 and 4, connection between the latter and the electrometer being broken. Now connect 2 to a potential U: there will be an induced charge on 1 and the electrometer will be deflected. The deflection in this will correspond to a charge σ_1 being given to the plate 1. The charge will also be given by $q_{21}U$, and combining this with (6) we have

$$\frac{Q_1}{\sigma_1} = \frac{u}{U}. \tag{11}$$

Thus the only quantities to be measured are the potentials U, u and u', and a sensitive electrometer of constant capacity can be used.

There are potentials of two orders of magnitude to be measured: one of the order of 1 volt and the other of the order of 100 volts. Voltages of both these orders, however, can easily be measured with an accuracy of 1 per cent. The low voltages were measured by comparison with a standard Weston cell. In practice the charges were not exactly neutralised, but the needle was brought very nearly back to the equilibrium position, and the small departures corrected for.

In order to reduce any small insulation leaks in the second chamber during the determination of the potential u, the charge Q_2 in this chamber could be nearly neutralised by changing the potential of the plate 4, and afterwards restored to its original value. By using this compensating method it was unnecessary to have the plates charged for any appreciable time, and therefore the effects of slight insulation leaks were reduced to a minimum. The manner in which the changes were brought about can be seen from the figure. The electrode B (fig. 1) was connected to the point *d*. When *a* and *b* and *b* and *d* were connected, B was at the potential of the plate M of the battery of cells. By breaking the contact between *a* and *b*, and joining *c* and *b*, the potential of B could be changed to that of the point N. P was a potentiometer consisting of 100 equal resistances. The current from a small number of accumulators passed through this, and, by moving round the pointer, any fraction of this small potential could be added to or subtracted from that of the battery. By connecting *d* to *e* instead of *d* to *b*, the potential of the electrode could be changed by a small known amount. This was used in measuring the quantity Q_1-Q_2. The potential of the electrode was determined by that of the battery. The small change of potential required to balance Q_1-Q_2 was measured by means of a potentiometer and a Weston cell.

An experimental difficulty may be noticed here. If the gas between the plates was ionised while the plate A was insulated and the plate B was connected to earth, a deflection corresponding to a positive charge was produced in the electrometer. This effect was not due to a difference in the coefficients of diffusion of the positive and negative ions because an effect of a similar order of magnitude was obtained in carbon dioxide, in which gas the coefficients of diffusion of the two kinds of ions are very nearly the same. The effect was probably due to the emission of electrons from the upper electrode under the influence of the Röntgen rays. It was shown, however, that this effect did not influence the results obtained. The charge received by the upper electrode, when a single flash of Röntgen rays was used, was measured for gradually increasing electric fields, first in one direction and then in the opposite direction. For small values of the electric field the curves obtained were unsymmetrical, but this lack of symmetry decreased very rapidly as the potential increased, and for the large fields used in these experiments the two curves for electric fields of opposite sign were identical.

4. *Preparation of the Gases and Vapours.*

The atmospheric air was thoroughly dried before being admitted to the apparatus by allowing it to remain in contact with phosphorus pentoxide for some time. The carbon dioxide was liberated by the action of hydrochloric acid on calcium carbonate and was dried by allowing it to remain in contact with phosphorus pentoxide for some time. The carbon monoxide was liberated by the action of sulphuric acid on formic acid and was dried over phosphorus pentoxide. The sulphur dioxide was obtained from a cylinder of the liquid and was dried over phosphorus pentoxide. The nitrous oxide was obtained from a cylinder of the gas and was dried over phosphorus pentoxide. In some cases the gases were passed through a spiral tube immersed in liquid air. The ionisation chambers were exhausted by means of a Töpler pump, and the remaining gas was absorbed by means of charcoal immersed in liquid air. The dry gas was then admitted to the apparatus. In every case great care was taken to make the gas or vapour dust-free.

5. *Experimental Results.*

In order to test the law of recombination and the general theory of Langevin's method the experimental conditions were varied over as wide a range as possible. Such variations were obtained in the following ways:—

1. Different samples of the gas were experimented on and the experiments were repeated after long intervals.
2. With a given ionisation the electric fields were varied as widely as possible.
3. The intensity of the ionisation for a given sample of gas at a given pressure was varied.
4. Both chambers in turn were used as the standard, and the sign of the electric field was reversed.
5. Experiments were made at different pressures.
6. The distribution of the ionisation was varied. In some cases there was little secondary ionisation: this was the case when the upper electrode was aluminium, and also when it was arranged that the radiation did not fall on the electrode. When brass was used there was a large amount of secondary ionisation.

The results are given in Table I. The figures in the second column give the value of the coefficient ϵ at the pressures given in the first column. The third column gives the quotient of ϵ by the pressure, and the numbers in this column are proportional to the coefficient of recombination over the range for which the mobility is inversely proportional to the pressure. In the fourth column is given the value of the quotient of ϵ by the square of the pressure.

Each result represents the mean of a large number of observations made under widely different conditions, and, in many cases, after long intervals of time. Under conditions so varied as those enumerated above it was only to be expected that some variations would occur: the greater number of these variations, however, were within 5 or 6 per cent. of the mean value.

The values apply to a mean temperature of about 15° C. The temperature at the time of the observations was always recorded, but no correction was made as it was considered that such a correction would almost certainly be within the limits of error of the experiment.

6. *Discussion of Results.*

From this table it will be seen that the coefficient ϵ is very nearly proportional to the square of the pressure over a fairly wide range of pressures. At higher pressures this rate of increase becomes smaller.

Table I.

Pressure in mm.	ϵ.	ϵ/p.	ϵ/p^2.
Air.			
743	0·272	368	495
662	0·215	325	491
644	0·204	318	494
462	0·104	226	488
363	0·067	182	508
307	0·050	161	530
197	0·019	96	490
Carbon Dioxide.			
729	0·529	725	996
614	0·390	635	1035
498	0·261	525	1054
373	0·151	406	1085
265	0·078	294	1110
175	0·038	217	1240
Carbon Monoxide.			
757	0·215	284	375
690	0·172	250	362
556	0·114	205	369
409	0·059	145	354
247	0·018	73	295
Sulphur Dioxide.			
680	0·765	1125	165
504	0·466	924	184
444	0·346	780	175
338	0·21	620	182
200	0·072	360	180
83·5	0·019	225	269
Nitrous Oxide.			
749	0·431	575	770
596	0·291	488	821
430	0·148	344	802
294	0·073	245	845
200	0·028	140	700

Such a departure is to be expected if we accept Langevin's interpretation of ϵ, for it would tend to approach a limit when every collision is accompanied by recombination. Under these circumstances ϵ would be unity, and a further increase in the pressure would produce no increase in the value of ϵ. This limit appears to be reached for comparatively small pressures:—in air at a pressure of about 4 or 5 atmospheres; in sulphur dioxide at an even lower pressure.

The Absolute Values of the Coefficient of Recombination.—The absolute values of the coefficient of recombination were calculated from the relation

$$\alpha = 4\pi(k_1+k_2)\,\epsilon e,$$

in which k_1 and k_2 are the mobilities of the positive and negative ions, and e is the electronic charge measured in electrostatic units. The mobilities have been determined with great accuracy for a large number of gases and vapours by Wellisch,[*] and the values determined by him were used. The values of α in terms of e are given in Table II. The results of Langevin and others on air and carbon dioxide at atmospheric pressure are also included in this table. The results are shown graphically in fig. 3.

Table II.

Air.

Pressure	743	662	644	462	363	307	197
Coefficient of recombination	3500	3090	3020	2150	1730	1530	920

Carbon Dioxide.

Pressure	729	614	498	373	265	175
Coefficient of recombination	3440	3020	2500	1930	1400	1020

Carbon Monoxide.

Pressure	757	690	556	409	247
Coefficient of recombination	1820	1600	1310	930	468

Sulphur Dioxide.

Pressure	680	504	444	338	200	83·5
Coefficient of recombination	2740	2250	1900	1510	876	548

Nitrous Oxide.

Pressure	749	596	430	204	200
Coefficient of recombination	2830	2400	1690	1110	690

	Air.	Carbon dioxide.
Townsend	3420	3500
McClung	3384	3492
Langevin	3200	3400

There is a good agreement between the results obtained by different observers working with air and carbon dioxide at atmospheric pressure. This is more striking when one considers the great difference between the method employed in the experiments described in this paper for example, and that employed by McClung.

At low pressures, however, there are wide divergences. From the curves

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[*] 'Phil. Trans.,' A, vol. 209.

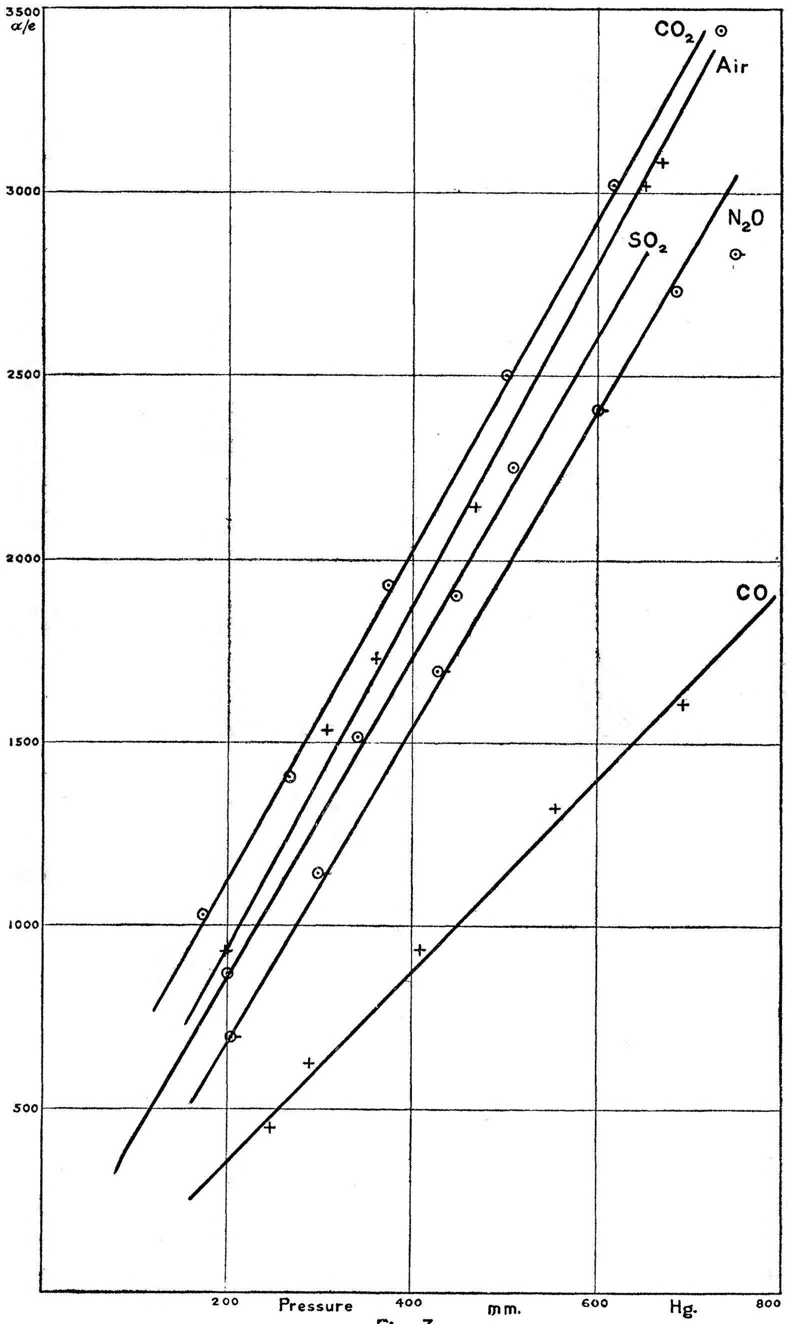

Fig. 3.

it can be seen that, for a considerable range of pressure, depending on the gas, the coefficient of recombination is proportional to the pressure. This range seems to be less in the case of those gases for which ϵ is large. At higher pressures, we have seen that ϵ approaches a maximum value equal to unity. The mobility of the ion, however, as Kovarik* has shown, varies inversely as the pressure over a range of pressures of 50 atmospheres. Thus the curve connecting the coefficient of recombination with the pressure will, at first, be a straight line, and afterwards will pass through a maximum value. At high pressures a very small value for the coefficient would be expected.

Many years ago Bragg showed that, in the case of the recombination of the ions produced by α-rays, there existed certain peculiarities in the initial stages of the recombination. Plimpton has very recently shown that similar peculiarities occur when the ionising agent is Röntgen rays. The abnormally high results obtained by these authors are very probably due to the fact that, in the initial stages, the ions are confined along the tracks of the electrons ejected from the molecules and, in general, the distance between an initial pair of ions would be less than the distance between the ions at a later stage.

In the method employed in the experiments described in this paper, this effect does not come in to any appreciable extent. In the first place, a uniform distribution of ions is unnecessary, and in the second place, the peculiar distribution of the ions characteristic of the ionisation by the moving particles ejected by the Röntgen rays would disappear almost instantaneously in the presence of the large electric fields used. This is supported by the agreement between the results of the experiments made under different experimental conditions; large variations of the electric field and of the intensity of the ionisation do not seem to produce any appreciable effect on the coefficient of recombination. Although for this reason the results obtained by Plimpton cannot be compared with those described here, one point may be noticed. As would be expected, Plimpton's values are in every case very large, but these values decrease when the time-interval during which diffusion is allowed to take place is increased. The final slopes of the curves obtained from Plimpton's data, however, are too steep to enable one to deduce a limiting value with any degree of accuracy. This is especially so in the case of carbon dioxide, in which the coefficient of diffusion is much smaller than it is in air. The final value obtained is 4880 compared with an initial value of 10,000, and the value is still decreasing. In the case of air the lowest value for α is 3960. This value is about 10 per cent. higher than the result given here.

The values of ϵ obtained at low pressures in these experiments may be briefly mentioned here. The observations at low pressures are much more difficult than those at higher pressures, especially in those gases in which the ionisation is small. The important quantity which has to be measured is $Q_1 - Q_2$, the difference between the quantities of electricity which reach the electrode for two different values of the field. This quantity depends on the value of the coefficient ϵ and on the ionisation in the gas. Both these decrease when the pressure decreases, the former being approximately inversely proportional to the square of the pressure. At low pressures, therefore, the difference $Q_1 - Q_2$ becomes very small. This difficulty can be obviated to some extent by using more than one flash of the rays, but this is not so satisfactory.

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* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 154.

The results obtained do seem to indicate departures from the linear law at lower pressures, but in view of the increased difficulty of the experiments it is perhaps well not to lay too much emphasis on these variations. It is significant, however, that the changes appear in the region of pressure in which other experiments seem to suggest that some modification takes place in the negative ion.

The constancy of the results that have been obtained in these experiments under conditions which have been very widely varied seems to be in favour of the simple law of recombination

$$\frac{dn}{dt} = -\alpha n^2,$$

or in its more general form,

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = \frac{dn_2}{dt}.$$

Among the modifications of this law which have been proposed, perhaps the best known is that of Sutherland

$$\frac{dn}{dt} = -\alpha n^{5/3}.$$

It is not always easy to distinguish between these two laws, and the results of some observers seem to fit in almost equally well with both formulæ. Experiments in which ionisation of very widely varying intensity is used seem most promising. It is hoped to give a more detailed account of some experiments on this point at a later date.

7. *Conclusions.*

(1) Recombination appears to take place according to the simple law

$$\frac{dn}{dt} = -\alpha n^2,$$

or more generally

$$\frac{dn_1}{dt} = -\alpha n_1 n_2 = -\frac{dn_2}{dt}.$$

(2) The coefficient of recombination varies with the pressure and throughout a considerable range of pressure is proportional to the pressure.

In conclusion I desire to express my appreciation of the kindly interest which Prof. Sir J. J. Thomson has shown throughout this work.

The Flexure of Telescope Mirror-discs Arising from their Weight, and its Influence upon Resolving Power.

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The resolving power of a reflecting telescope is proportional to its aperture, the mirror being supposed accurately a paraboloid of revolution, so that a bundle of parallel rays pass through a geometrical focus after reflection. Regarded from this point of view alone it is of advantage, in the construction of a reflecting telescope, to make the mirror of as large a size as the mechanical difficulties incident to the construction of large mirrors will allow, difficulties, that is to say, such as that of obtaining the glass of the necessary homogeneity throughout, in order to avoid distortion owing to changes of temperature, and the difficulties of grinding, shaping, and polishing. There is, however, another factor to be considered which affects the problem. The mirror, even if perfect in other respects, will, when partially supported, be distorted by its weight, to a greater or less extent according to the nature of the support. This distortion will cause a diminution in the resolving power, the effect of which will evidently increase with the size of the mirror, and so will tend to counteract the advantage accruing from the larger aperture. It is conceivable even that there will, for any